

Message

From: Beck, Nancy [Beck.Nancy@epa.gov]
Sent: 4/23/2019 9:36:02 PM
To: Bertrand, Charlotte [Bertrand.Charlotte@epa.gov]; Keller, Kaitlin [keller.kaitlin@epa.gov]; Baptist, Erik [Baptist.Erik@epa.gov]
Subject: RE: Drinking Water Follow-up

The oxon is what causes the Ache inhibition at the nerve junctions in the body (but not necessarily the brain). Interestingly, the oxon doesn't enter the brain but I believe some very low levels have been detected—need to double check that. I believe chlorpyrifos can enter the brain and then it can break down to the oxon-I think very slowly, but the oxon itself cant get in. orally if you give the oxon- no effect as it cant get past the liver..

Nancy B. Beck, Ph.D., DABT
Principal Deputy Assistant Administrator, OCSP
P: 202-564-1273
beck.nancy@epa.gov

From: Bertrand, Charlotte
Sent: Tuesday, April 23, 2019 5:33 PM
To: Beck, Nancy <Beck.Nancy@epa.gov>; Keller, Kaitlin <keller.kaitlin@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>
Subject: RE: Drinking Water Follow-up

What's the toxicity of the oxon? I was surprised to hear today that it is more toxic than chlorpyrifos.

From: Beck, Nancy
Sent: Tuesday, April 23, 2019 1:40 PM
To: Keller, Kaitlin <keller.kaitlin@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>
Subject: RE: Drinking Water Follow-up

So we know chlorination has a large impact—converts 100% to the oxon which is very short-lived.

From the 2000 SAB snippet they provided- see highlight below. Why are we using surface water for this pesticide??

Question 2.7 Based on this technical review, OPP is leaning toward an interim approach to address the impacts of water treatment on a case-by-case, pesticide-specific basis in its human health risk assessment. OPP expects that for most pesticides, however, available data will not be sufficient to establish the impacts of treatment. Accordingly, as a practical matter, it is very likely that until pesticide-specific treatment data are generated, OPP will be using raw or untreated drinking water estimates in human health risk assessments under FQPA. Given the objective of estimating pesticide concentrations in drinking water, does the SAP believe that the state-of-the-science supports this approach? If not, how would an approach be developed based on the state of knowledge about the impact of treatment on pesticides?

The Panel agreed that this is the only feasible approach. Until adequate research is conducted, it would be prudent for the Agency to take a conservative approach by assuming that the finished water pesticide concentration is the same as that estimated for the raw water source. Exceptions might be made for two or three pesticides if the Agency's review demonstrates that removal due to chlorination or hydrolysis can be relied upon. It is also prudent to assume that the health effects of pesticide treatment transformation and disinfection byproducts are similar to those of the parent pesticides.

Nancy B. Beck, Ph.D., DABT
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From: Keller, Kaitlin
Sent: Tuesday, April 23, 2019 1:31 PM
To: Beck, Nancy <Beck.Nancy@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>
Subject: RE: Drinking Water Follow-up

Responses in red.

So when we do an FQPA evaluation to look at contributions from food and water, does the program use surface water levels and not levels from monitored drinking water?

Yes

What do we do generally and what was done in the evaluation of chlorpyrifos?

Since we have chemical specific information on the formation of the oxon as a result of drinking water treatment for chlorpyrifos, we considered exposure to the oxon as well chlorpyrifos. Generally, we do not have drinking water treatment data and would therefore rely on the estimates in surface water.

I was hoping to see how we get from surface water to drinking water, but it sounds like that we do not model that piece.
Correct

From: Beck, Nancy
Sent: Tuesday, April 23, 2019 11:35 AM
To: Keller, Kaitlin <keller.kaitlin@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>
Subject: RE: Drinking Water Follow-up

Thanks.

So when we do an FQPA evaluation to look at contributions from food and water, does the program use surface water levels and not levels from monitored drinking water?

What do we do generally and what was done in the evaluation of chlorpyrifos.

I was hoping to see how we get from surface water to drinking water, but it sounds like that we do not model that piece.

Thanks.

Nancy B. Beck, Ph.D., DABT
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From: Keller, Kaitlin

Sent: Tuesday, April 23, 2019 11:30 AM

To: Beck, Nancy <Beck.Nancy@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>

Subject: RE: Drinking Water Follow-up

Nancy—here's the response back. Looking at a small meeting with the team, possibly Monday. Let me know if you have other questions to send in advance.

Question: At the meeting last week, I think it was Rochelle that mentioned we do take our surface water modelling to the drinking water level.

Can I see what those values look like in comparison to data we have from sources such as CCL4, USDA finished water data sources, and USGS NWQA.

Response: In the meeting last week, Rochelle was specifically referring to the consideration of the conversion of chlorpyrifos to chlorpyrifos-oxon that happens when water is chlorinated. Free chlorine is frequently used to disinfect source water, and studies have shown that the conversion can approach 100%. Some treatment facilities don't use free chlorine, but may use chloramines to disinfect, and the conversion to oxon is much less when chloramines are used. Thus, in the drinking water assessment, we provided results accounting for 100% conversion to oxon, and 0% conversion to oxon.

Very limited data on physical removal processes such as coagulation/flocculation, sedimentation, and filtration are available for chlorpyrifos or chlorpyrifos-oxon. However, such processes, with the exception of granular activated carbon⁵³, have been shown to be ineffective for select organic pesticides.⁴³ Based on the physical-chemical properties of chlorpyrifos and chlorpyrifos-oxon, granular activated carbon likely reduces the amount of both chemicals to some extent. One study shows addition of powder activated-carbon reduces the amount of chlorpyrifos by ninety percent.⁴⁹ However, data are not available on the exact removal efficiency for chlorpyrifos-oxon treated with granular activated carbon or powder activated carbon. Generally, carbon sources are added early in the treatment process. It should be noted that granular activated carbon is not a common treatment practice for all treatment facilities. Additionally, powdered activated carbon, which is used for taste and odor control, is not used year round.

⁴³ U.S. Environmental Protection Agency, Office of Pesticide Programs. The Incorporation of Water Treatment Effects on Pesticide Removal and Transformations in Food Quality Protection Act (FQPA) Drinking Water Assessment, October 25, 2001

⁴⁹ Ormad, M. P., Miguel, N., Matesanz, J. M., Ovelleiro, J. L., Chemosphere, 2008, 71 97-106

⁵³ U.S. Environmental Protection Agency. 1998. Small System Compliance Technology List for the Non-Microbial Contaminants Regulated Before 1996. EPA 815-R-98-002.

Without knowing how much is removed, we cannot reliably estimate what impact, if any, drinking water treatment would have on the chlorpyrifos concentrations coming into the treatment plant from source water. Thus, OPP relies on model-estimated and monitored source water concentrations for its human health risk assessment. Pasted below is an excerpt from an SAP report in 2000 that summarizes the state of the science regarding drinking water treatment and how OPP addresses these uncertainties.

In terms of finished water monitoring programs, the chlorpyrifos DWA does speak to those results. For systems using free chlorine, which is quite common, chlorpyrifos would not be expected to be found in finished drinking water because it would have been converted to the oxon. What we also found was that the sample frequency of these programs, often just quarterly samples are taken, is insufficient to draw any conclusions on estimating 21-day average concentrations that people could be exposed to in their drinking water. There's too much time in between sampling events to capture the potential chlorpyrifos or chlorpyrifos-oxon in the sampled water. With just four samples taken per year, it is unlikely to detect a pesticide that is sporadically applied and degrades with time, unless the sampling event was timed in order to specifically capture an application and runoff events.

Excerpt from SAP report on drinking water process

Question 2.7 Based on this technical review, OPP is leaning toward an interim approach to address the impacts of water treatment on a case-by-case, pesticide-specific basis in its human health risk assessment. OPP expects that for most pesticides, however, available data will not be sufficient to establish the impacts of treatment. Accordingly, as a practical matter, it is very likely that until pesticide-specific treatment data are generated, OPP will be using raw or untreated drinking water estimates in human health risk assessments under FQPA. Given the objective of estimating pesticide concentrations in drinking water, does the SAP believe that the state-of-the-science supports this approach? If not, how would an approach be developed based on the state of knowledge about the impact of treatment on pesticides?

The Panel agreed that this is the only feasible approach. Until adequate research is conducted, it would be prudent for the Agency to take a conservative approach by assuming that the finished water pesticide concentration is the same as that estimated for the raw water source. Exceptions might be made for two or three pesticides if the Agency's review demonstrates that removal due to chlorination or hydrolysis can be relied upon. It is also prudent to assume that the health effects of pesticide treatment transformation and disinfection byproducts are similar to those of the parent pesticides.

A water treatment operator will have to treat drinking water removal of pesticides when and if they are found in the source water at concentrations above established MCLs. Therefore, any exceedence in source water imposes an economic burden on a drinking water treatment plant beyond the costs of simple conventional drinking water treatment. The operation of a responsible water system may require monitoring for pesticides used on its watershed even if there is not an established MCL, especially if consumers of that drinking water are aware it is being used and suspect the possibility of contamination. Adjustments for pesticides based on water treatment should be undertaken only if a broad-scaled monitoring program were initiated which carefully evaluated the effectiveness of drinking water treatment methods to dependably remove those pesticides that are frequently found in water. Such a monitoring effort would have to be aimed at the questions of how different unit processes contributed to removal. It would need to be focused on developing a set of criteria for pesticides that fall into particular chemical and physical classes. It would necessitate developing enough data that the statistical confidence of the estimated removal can be stated with some accuracy with clear description of the conditions that were in existence at each plant. This is a situation where inadequate data could be dangerous. Therefore, such a study should not be undertaken lightly. Paired sampling monitoring programs would provide better data.

There is a longer-term approach that could address issues of variability (not necessarily solve them) that should be considered. Manufacturers of pesticides could be required to develop chemical-specific methods for treating water intended for human consumption that might exceed an allowable limit. That information should be compiled and made available to water plant operators in the event of imprecise predictions based on models that do not capture the variables that could be encountered in a specific location.

This is more than a health issue; it is a question of how much confidence people can/will place in their local sources of drinking water. Applications of material on a watershed should not be done without the knowledge of systems drawing water from the bodies of water affected.

The Panel's concurrence with the Agency proposal is offered primarily because of the absence of information. It should not be taken as an endorsement for the absence of a serious program monitoring field-scale treatment performance. Monitoring the drinking water levels of those pesticides that have been shown to occur in raw water supplies should be among EPA's highest priorities.

One Panel Member noted that, looking to the future, there is a potential for a more accurate estimate of the levels of pesticides in drinking water treatment in the future on a national basis. This could be enabled by three factors: 1) further development of the models for estimating pesticide concentrations in raw water, 2) the emergence of a national database on our water treatment plants and the process train each plant uses, and 3) more extensive characterization of empirical performance of these treatment trains in removing specific pesticides. The time may not be far off when models such as those shown today project the distribution of pesticide densities in the environment at large. It also seems that data collected on pesticides in raw and finished water could be used, along with the specific treatments used to produce finished water at each site, to produce similar models characterizing the removal of these pesticides in treatment. Finally, the results of both of these models could be combined with the national water treatment plant database to produce national estimates of exposure. Such an effort would seem to be in character with the scope of the OPP modeling effort that we have already seen presented today.

The current state of the science does support using raw-water data to estimate treated- water concentrations. However, this must result in large error bars, owing to the wide range of removal rates and rates of production of transformation products, some of which may be 20 times as toxic as the parent compound. EPA should put a high priority on additional research on the effects of drinking-water treatment on pesticide and degradate concentrations. Case-by-case studies of individual pesticides are prone to ignore the risk posed by exposure to mixtures of various pesticides, degradates, and other contaminants.

From: Beck, Nancy
Sent: Monday, April 22, 2019 7:29 AM
To: Keller, Kaitlin <keller.kaitlin@epa.gov>; Keigwin, Richard <Keigwin.Richard@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>
Cc: Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>; Anderson, Brian <Anderson.Brian@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>
Subject: RE: Drinking Water Follow-up

Thanks to the team. This is very helpful.

At the meeting last week, I think it was Rochelle that mentioned we do take our surface water modelling to the drinking water level.

Can I see what those values look like in comparison to data we have from sources such as CCL4, USDA finished water data sources, and USGS NWQA.

Nancy

Nancy B. Beck, Ph.D., DABT
Principal Deputy Assistant Administrator
Office of Chemical Safety and Pollution Prevention
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From: Keller, Kaitlin
Sent: Friday, April 19, 2019 10:00 AM
To: Beck, Nancy <Beck.Nancy@epa.gov>; Keigwin, Richard <Keigwin.Richard@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>
Cc: Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>; Anderson, Brian <Anderson.Brian@epa.gov>
Subject: RE: Drinking Water Follow-up

Nancy—responses from the team are below with two additional responses based on our conversation yesterday. Let me know if you want a brief meeting/call next week if you have additional questions.

Why do we compare our modelled data to surface water. Since people are not supposed to drink surface water, shouldn't we care about what's in treated drinking water or groundwater? What would that comparison look like?

The chlorpyrifos drinking water assessment focused on surface water because chlorpyrifos is much less likely to contaminate groundwater due to its environmental fate properties. Surface water that is sourced for drinking water includes rivers, streams, and impoundments such as reservoirs. Community water system intakes are distributed across the 21 major water resource regions located in the United States, 18 of which are within the conterminous states.

Drinking water treatment methods such as sedimentation, flocculation, chlorination, and filtering through granular or powdered activated carbon can impact which pesticide residues and at what levels, people can be exposed to in their tap water. Treatment methods primarily focus on addressing taste and odor and vary in their effectiveness in removing pesticides. In addition, which treatment methods are used, and in what order, varies across community water systems. Treatment methods also vary over time, even at a single treatment plant. Because of this variability in treatment methods, and the lack of data on the effectiveness of treatment in removing pesticides, drinking water treatment adds another layer of complexity in estimating potential exposure to pesticides and associated transformation products.

Because drinking water for a large percentage of the population is derived from community water systems that treat raw water¹ prior to consumption, the impact of water treatment on pesticide removal and transformation are considered, when possible, in estimating drinking water exposure.^{2,3,4} However, in practice, drinking water treatment is not commonly considered in drinking water assessments for the reasons discussed above.

Therefore, EFED uses modeling and monitoring data to estimate pesticide concentrations in source surface water, and where possible, considers drinking water treatment effects. In terms of the chlorpyrifos drinking water assessment, chlorination, a commonly used drinking water treatment, was evaluated. There are studies showing that chlorpyrifos is almost completely converted to chlorpyrifos-oxon when drinking water is treated with free chlorine. Yet, under a different disinfection process using chloramines, the percent conversion of chlorpyrifos to chlorpyrifos-oxon is much lower. The 2016 chlorpyrifos DWA used a bounding approach to capture the range of potential exposures from 100% chlorpyrifos to 100% chlorpyrifos-oxon.

¹ United States Environmental Protection Agency. 1989. Technologies for Upgrading Existing or Designing New Drinking Water Treatment Facilities. EPA/625/4-89/023.

² Assessment of pesticide concentrations in drinking water and water treatment effects on pesticide removal and transformation, FIFRA Scientific Advisory Panel Meeting September 26-29, 2000

³ *Progress Report on Estimating Pesticide Concentrations in Drinking Water and Assessing Water Treatment Effects on Pesticide Removal and Transformation: A Consultation*. FIFRA Scientific Advisory Panel Meeting, Sept 29, 2000; SAP Report No. 2001-02. February 12, 2011.

⁴ U.S. Environmental Protection Agency, Office of Pesticide Programs. The Incorporation of Water Treatment Effects on Pesticide Removal and Transformations in Food Quality Protection Act (FQPA) Drinking Water Assessment, October 25, 2001

What is the half life of chlorpyrifos in water? Or do we use the soil metabolism half life in our models that get us surface water levels? Or do we use 91.2 (water column metabolism half life).

The half-life in water used for aquatic modeling for chlorpyrifos is 91.2 (accounts for uncertainty in only having one study). We also evaluated the impact of using 30.4 days (single study value) in a sensitivity analysis. This value was derived from a laboratory aerobic aquatic metabolism study, which is conducted in a vessel with water over sediment.

How does the 90-day aquatic modeling half-life relate to the oxon? The 90-day aquatic half-life (which is 3x the actual study half-life to account for having just one study) represents the degradation of chlorpyrifos to other transformation products. In fact, we don't see the oxon formed in our battery of environmental fate studies. The oxon does form, however, during drinking water treatment with chlorine. We agree that once formed during drinking water treatment, the oxon does break down faster.

Why not use the UMCr data (finished water monitoring) for parent and extrapolate to the oxon? The UMCr finished water monitoring is conducted at a small subset of facilities and only four samples are taken over the course of one year. Given that the duration of interest for chlorpyrifos and chlorpyrifos oxon is a 21-day average concentration, this amount of sampling is not enough to capture the concentrations that could be occurring in finished drinking water. This interpretation has been supported by the SAP. In addition to sampling frequency, other factors such as whether chlorpyrifos is used in the watershed and if so, when, vulnerability of the watershed, etc. lead to uncertainty in relying on this type of monitoring –we do not know if chlorpyrifos would be expected to occur in the water samples. If we did have reliable monitoring data, we could make some assumptions to extrapolate those concentrations to the oxon.

From: Beck, Nancy

Sent: Thursday, April 18, 2019 7:47 AM

To: Keigwin, Richard <Keigwin.Richard@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>

Cc: Keller, Kaitlin <keller.kaitlin@epa.gov>; Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>; Anderson, Brian <Anderson.Brian@epa.gov>

Subject: RE: Drinking Water Follow-up

Many thanks to the team.

I have only just skimmed but a few questions:

- Why do we compare our modelled data to surface water. Since people are not supposed to drink surface water, shouldn't we care about what's in treated drinking water or groundwater? What would that comparison look like?
- What is the half life of chlorpyrifos in water? Or do we use the soil metabolism half life in our models that get us surface water levels? Or do we use 91.2 (water column metabolism half life).

Thanks!

Nancy B. Beck, Ph.D., DABT

Principal Deputy Assistant Administrator, OCSP

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From: Keigwin, Richard
Sent: Thursday, April 18, 2019 6:49 AM
To: Beck, Nancy <Beck.Nancy@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>
Cc: Keller, Kaitlin <keller.kaitlin@epa.gov>; Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Messina, Edward <Messina.Edward@epa.gov>; Anderson, Brian <Anderson.Brian@epa.gov>
Subject: RE: Drinking Water Follow-up

Nancy—

Attached are EFED's responses to your questions.

--Rick

From: Beck, Nancy
Sent: Friday, April 12, 2019 2:16 PM
To: Messina, Edward <Messina.Edward@epa.gov>
Cc: Keller, Kaitlin <keller.kaitlin@epa.gov>; Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Keigwin, Richard <Keigwin.Richard@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Dunn, Alexandra <dunn.alexandra@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>
Subject: RE: Drinking Water Follow-up

Ed,
Many thanks for this.

A few questions:

- Is there a larger technical support document or the water modelling approach we have used in the most recent assessment (2016?)
- Is there a chart/data set/spreadsheet comparing modelling and monitoring data?
- Can we benchmark mean, medium and high end levels against aquatic LC50s? From the monitoring and the modelling?
- In the modelling what do we assume about half life of chlorpyrifos? My understanding is that its oily and partitions to soil, does that mean water half life is super short. So I guess also what is the Koc that is used.

Btw, Marietta and Brian did a great job this morning at the ESA meeting. All the teams hard work is going to continue to pay off in the ESA world!!

Thanks,
Nancy

Nancy B. Beck, Ph.D., DABT
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From: Messina, Edward
Sent: Friday, April 5, 2019 4:50 PM
To: Beck, Nancy <Beck.Nancy@epa.gov>
Cc: Keller, Kaitlin <keller.kaitlin@epa.gov>; Dinkins, Darlene <Dinkins.Darlene@epa.gov>; Keigwin, Richard <Keigwin.Richard@epa.gov>; Echeverria, Marietta <Echeverria.Marietta@epa.gov>; Miller, Wynne <Miller.Wynne@epa.gov>; Dunn, Alexandra <dunn.alexandra@epa.gov>; Baptist, Erik <Baptist.Erik@epa.gov>; Bertrand, Charlotte <Bertrand.Charlotte@epa.gov>
Subject: Fwd: Drinking Water Follow-up

Nancy,

As requested.

Have a great weekend,
Ed

Ed Messina
Acting Deputy Office Director (Programs)
Office of Pesticide Programs
U.S. EPA
(703) 347-0209

Begin forwarded message:

From: "Echeverria, Marietta" <Echeverria.Marietta@epa.gov>
To: "Keigwin, Richard" <Keigwin.Richard@epa.gov>, "Messina, Edward" <Messina.Edward@epa.gov>, "Miller, Wynne" <Miller.Wynne@epa.gov>
Cc: "Spatz, Dana" <Spatz.Dana@epa.gov>, "Bohaty, Rochelle" <Bohaty.Rochelle@epa.gov>, "Anderson, Brian" <Anderson.Brian@epa.gov>
Subject: FW: Drinking Water Follow-up

Rick/Wynne/Ed – The latest chlorpyrifos materials requested by OCSPP-IO. Let us know if you have comments/questions.

Thanks,
Marietta

From: Spatz, Dana
Sent: Thursday, April 04, 2019 6:58 PM
To: Echeverria, Marietta <Echeverria.Marietta@epa.gov>
Cc: Anderson, Brian <Anderson.Brian@epa.gov>; Bohaty, Rochelle <Bohaty.Rochelle@epa.gov>; Spatz, Dana <Spatz.Dana@epa.gov>
Subject: RE: Drinking Water Follow-up

Marietta,

Attached, please find 4 files addressing the request for information on drinking water refinements, peer review of methods, and mitigation options relative to the chlorpyrifos drinking water assessment.

1. Drinking Water Assessment Tiering and Chlorpyrifos Refinements
2. DWA Peer Reviews
3. Mitigation Ideas

4. Presentation to CLA on the tiered drinking water assessment process

A big thank you to Rochelle for pulling this together so quickly.

Please let me know if you have any questions, comments, or edits.